THE MEANING OF THE BASICITY OF GLASS MELT
AND ATTEMPTS TO MEASURE IT.   PART II

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16. Abstract

The basicity relations of a few simple glass systems -- Li, Na, K -- are studied. EMF values were obtained by pouring two different glass melts into a ceramic crucible. The potential curves of all three glasses (EMF plotted against Mol-% alkali) had essentially the same character: at first they are flat, then climb radically and finally are flat again. Variations in the potential curves were explained in terms of molecular structure, in particular the various ion field strengths. Changes in basicity were studied with a color indicator (CoO for low alkali regions, S for high alkali regions). Only the order of basicity could be determined; it was not possible here to ascertain if a melt was acidic or basic, or where an actual neutral point would lie.

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THE MEANING OF THE BASICITY OF GLASS MELT AND ATTEMPTS TO MEASURE IT.   PART II[1]

(Report from the Kaiser Wilhelm Institute for Silica Research, Berlin-Dahlem)

W. Stegmaier and A. Dietzel

D. Electrochemical Measurements   *

Melting tests with color indicators make possible the comparison of the relative basicity in various material systems. Using this procedure, however, it was not possible at the outset to determine a coefficient for the absolute degree of basicity in any given melt. The primary means for making a direct measurement of basicity was the electrochemical potential measurement of galvanic concentration chains. Such chains were created and measured by H. Lux [7][2] in melted salts. They were also used independently by P. Csaki and A. Dietzel [20] to measure the inner partial pressure of oxygen. H. Lux used the following chains: reference electrode was platinum or gold (air) in a melt of an eutectic mixture of Na_2SO_4 and K_2SO_4. The other electrode was submerged in the same eutectic mixture, to which various quantities of other materials such as Na_2O, Li_2O, $Na_2B_4O_7$, Al_2O_3, $NaPO_3$ were added. These chains yielded reproducible potentials, which allowed the quantities and anticipated basicities of the admixed material to be determined. At first Lux was unable to make a thorough-going interpretation of the potentials. Even though his report was published under the title of "The Determination of Oxygen Ion Concentrations," Lux admitted that the determination of the potentials in the sense of an electromotor activation of the oxygen would run into serious difficulties.

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[1]For Part I of this work, cf. Glastechn. Ber.18/11, 297-308 (1940).

[2]Translator's note: Notes 7-37 missing in original.]

*Numbers in margin indicate pagination in the foreign text.

Most probably, the Na_2O disassociated into Na vapor and Na_2O_2 and the Na built a sodium alloy potential with the metal electrode. No reason was given for this. Also missing was a discussion of whether or not and in what sense diffusion potentials influenced the measurements.

The goal of the work from P. Csaki and A. Dietzel was to determine the inner partial pressure of oxygen in the second borax melt from the EMF of the chain Pt (O_2)/borax melt in (O_2)/ borax melt in gas x/Pt (Gas x). The Nernstian formula could be used to make calculations with satisfactory exactitude. This states that the determining potential on the platinum electrode is determined through the process:

$$O + 2 \ominus \rightarrow O''$$

or through a similar process:

$$(B. \ B_2O_3 + 2 \ominus + O \rightarrow 2 BO'_2).$$
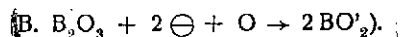
When the simple electrochemical laws in this experiment could be used with variable P_{O_2} and constant $C_{O''}$ of the melt, then they can also be used with variable $C_{O''}$ and constant P_{O_2}. In the following experiments a concentration potential had to be formulated, if two platinum electrodes rinsed with oxygen of unknown pressure t are suitably placed in two melts of differing basicity and both melts are brought into electrical contact. This arrangement contains a number of steps, which were, in part, difficult to realize.

1. Arrangement of the experiment. Completely unambiguous was the use of platinum electrodes and the use of air and rinsing with constant oxygen pressure (compare Csaki and Dietzel). Difficulties arose from two factors, namely, the crucible material and the way in which the two melts were connected.

Building upon the experiences of Csaki and Dietzel who found the potential to be detrimentally affected by the dissolving of ceramic parts, it was not even attempted to use ceramic materials for the arrangement of the chains. The first arrangement consisted of both melts being placed in a platinum crucible next to each other. Both melts were poured in the form of the half-crucible and placed vertically next to one another in the crucible or else they were poured simultaneously into the crucible. It was shown, however, that at temperatures from 700-800°C the viscosity, especially that of the sodium-rich borate melt was so low that within a short time the two melts mixed with each other. This was made visible by coloring one of the melts with a trace of CoO. The result was an exceptionally large fluctuation of the potential. In the next experiment the melts were filled in two platinum crucibles and connected with a band, as was done by Csaki and Dietzel. According to the band used (usually glass, borosilicate glass, boric acid glass or borax glass in platinum tubes, etc) a different and usually inconstant potential was obtained. This was caused by the band substance mixing with both melts and temporally variable diffusion potentials, which could not be reproduced were created on the surface of contact. It was hoped that the disadvantages of the easy miscibility could be avoided by carrying out the potential measurements at lower temperatures at which the resulting higher viscosity would make a mixture more difficult. Here new complications set in. At 450-550° other experimental arrangements were used, e.g., two glass plates fused to each other into which platinum electrodes were melted. But here too no temporally constant potential could be obtained. At first it was believed that the rinsing of the submersed electrode with oxygen was insufficient for the now highly-viscous melt. A thin platinum layer applied by cathodic sputtering which allowed the oxygen to enter from the rear surface through the platinum covering through to the contact surface resulted in no improvement. Most probably the fluctuating potential can be traced to a crystallization process on the

surface of the electrode. As a matter of fact, crystal precipitants tend to appear on the surface layer. While the precipitated crystals were either alkali rich or poor according to the combination of the melts, the potentials were clearly determined by the basicity of the "mother-liquor" on the electrode with continually changing, undefined combinations. The appearance of these crystallizations which cannot be avoided on glasses in the undercooling domain was the cause for undertaking the later potentiometric measurements at higher temperatures, (850°), where all crystal buildup was excluded at the beginning in this system. At lower temperatures it was observed that when a common glass cover was placed between the two melts to be measured as a diaphragm, rather than placing them immediately against each other, the observed potential was significantly higher. It can be seen that the use of a diaphragm causes additional potentials (clearly surface potentials) to be created, the evaluation of which has not yet been accomplished.

2. Carrying out the experiment. After the above arrangements failed to give a temporally constant potential the following arrangement was made with ceramic material at 800-850°C with little hope for success (Fig. 7). The two different melts were poured into a crucible in an electric oven. The crucible was made of sintered corundum, later from hard porcelain, which was divided into two halves by a separating wall from the same material. The crucible was 35 mm high with an outer upper diameter of 41 mm, a lower diameter of 20 mm. The height of the separating wall was 35 mm. The platinum electrodes were submerged 2 mm deep in the middle of both melt surfaces.

Surprisingly, with this arrangement an EMF could be measured which, after the temperature equalization after about 10 or 15 minutes remained satisfactorily constant for hours. Not once was it necessary to bring the two melts into electrical contact by laying a borax thread over the separation wall. To

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the contrary, in order to prevent an undesirable blending both
sides were filled with only enough melt to bring the glass
surface about 6-8 mm under the edge of the separation wall. The
flow of current was affected by an electrode through the melt (1) --
dividing wall (2) -- to the other electrode. As an example
of the temporal variation of the potential the measurement of
the EMF of the chain plus Pt (air)/borate melt with
0.70 mol-% Na_2O/borate melt with 33.1 mol-% Na_2)/Pt (air) --
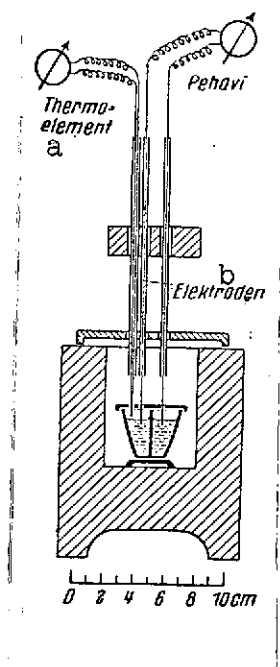is given.

The EMF was measured with a
"Pehavi" of Hartmann and Braun
(accurate to 2 mV) which was
sufficient for the intended use.
The temperature of the melt was
monitored by a calibrated thermal
element as shown in Fig. 7. With
this arrangement at 850°C the
potentials of the chain:

+Pt (air)/borate melt with 0.5-
0.7% R_2O/borate melt with
x% R_2O/Pt (air) --

in part also:

+Pt (air)/B_2O_3/borate melt with
x% R_2O/Pt (air) --

were measured. R_2O was used for
the alkali oxides Li_2O, Na_2O, K_2O.
The graduated concentrations x
lie between 0 and 40%. The melts
were made in platinum crucibles
partly in a gas oven partly in an
electrical oven (the different atmospheres in which the melts
stood before and during the measurements could not be noticed)
and were then poured into a porcelain crucible with a separation
wall. After the EMF measurements the melts were taken from

Fig. 7. Arrangements
of the experiments.
Key: a.   Thermal
           element
       b.   Electrodes

TABLE 3.   TEMPORAL VARIATION OF THE CONCENTRATION POTENTIAL
           IN THE DOUBLE CRUCIBLE ARRANGEMENT

Temper-ature	Time in minutes	EMF in V
900	0	0.685
900	1	0.730
900	3	0.755
890	4	0.765
885	5	0.769
875	8	0.783
865	12	0.785
860	13	0.785
855	15	0.786
852	18	0.786
852	21	0.785
850	25	0.785
845	30	0.785
850	35	0.785
850	40	0.785
850	42	0.785
850	49	0.785
850	56	0.785
850	60	0.785
850	75	0.785
850	95	0.785

around the electrode with a spatula and the R_2O content
of the melts was determined through dissolving in water
and titration with n/10 HCl against Methyl Orange as an
indicator.

3.   Results of the Measurement

With the above arrangement the following concentration
chains were measured:

1.   Total potassium borate glasses and boric acid against
a potassium borate glass with 0.56 mol-% K_2O;

2.   Total sodium glasses with boric acid against a sodium
borate glass with 0.70 mol-% Na_2O;

3.   Sodium diborate against potassium diborate;

4.   Total lithium glasses against B_2O_3.

In the beginning the conjecture that pure B_2O_3 would behave electrochemically fundamentally different than a borate melt for structural reasons was not ungrounded. Therefore the K and Na glasses were inserted in an alkali borate melt first. This was shown, however, to be unnecessary. The results of the calculations were the following:

From the chains

+Pt/borate glass 0.56 mol-% K_2O/borate glass 30.5 mol-%
     K_2O/Pt--;   EMF = $\pm$ 1.02 V

+Pt/borate glass 0.56 mol-% K_2O/B_2O_3/Pt--; EMF = $\pm$ 0.0 V
would result in the following:
     +Pt/B_2O_3/borate glass 30.5% K_2O/Pt-- an EMF = 1.02 V.

Analogously for

+Pt/borate glass 0.70 mol-% Na_2O/borax (33.1 mol-% Na_2O)/
     Pt--; EMF = + 0.76 V

+Pt/borate glass 0.70 mol-% Na_2O/B_2O_3/Pt --; EMF = -0.24 V
for the chain +Pt/B_2O_3/borax/Pt --; EMF = +1.00 V.

If instead of placing the potassium glass against the B_2O_3 and the sodium glass (borax) against the B_2O_3, both the K and Na borate glasses were placed against another it can be expected that the chain

+Pt/borate glass 3.05 mol-% K_2O/borate glass 33.1% Na_2O
(borax)/Pt --

would possess an EMF of +0.02 V.   In actuality after 20 minutes
a constant value of +0.15 V was measured.   Taken absolutely
the agreement is not good;   in view of the possible mistakes
in measuring such alkali-rich chains resulting from crucible
dissolution (see later), however, it can be seen as satisfactory,
especially in view of the fact that small differences are observed
here in very high EMF values.

Since such a calculation of the EMF values for pure
B_2O_3 is clearly reliable, the use of a lithium borate melt as
a control melt for the Li glasses was omitted.   All lithium
glasses were, therefore, measured against B_2O_3.

In order to compare all the measurement results in
Fig. 8, all the measurement results were related to Pt/B_2O_3 as
a comparison half-element; i.e., 0.24 V were added to the
actually measured EMF values in the sodium glasses, while in the
potassium series no change was necessary.   As can be seen in
Fig. 8 there are three naturally occurring curves which fall
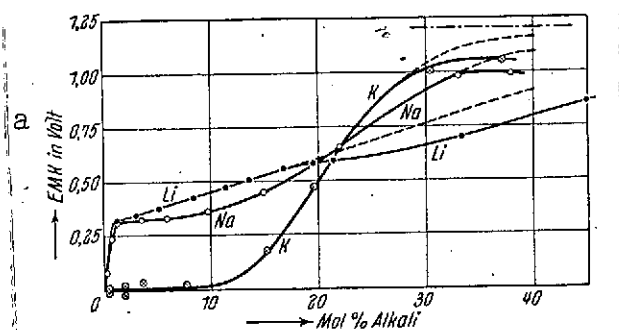sharply to pure B_2O_3 melts.

Fig. 8.   Potential curves for
Li - Na - K borate melts against
pure B_2O_3.

Key: a.   EMF in volts

4.   Interpretation of the
Potential Curves.

As can be seen in Fig. 8
the potential curve of Li,
Na and potassium borate glasses
have essentially the same
character: at first they are
flat, then climb radically
and finally are again flat;
but 3 alkalies show clear
differences.   It is emphasized
that these variations are not

the result of measurement inexactitude since they could be
reproduced on specially prepared new melts; the deviations were
in the range of 5-10 mV. The various curve paths must have a
deeper, real meaning. An attempt to interpret the potential
curves should be attempted on the basis of our present knowledge
of the molecular structure of the borate glass.

Three areas can be seen on the curves especially those of
the sodium and potassium borate. The first section extends from
0% to approximately 10% R_2O; it is characterized by an almost
horizontal path of the potential curves, possibly after a radical
climb in the beginning. After this beginning climb the curves
lie at various heights. It cannot be mistaken that the arrangement
of the curves in the order Li - Na - K contains a certain
regularity. In the second area the curves climb steeply and to
a different degree for each alkali, but inversely from the
beginning curve: the K_2O curve climbs the steepest, the Na_2O
curve runs somewhat more level and the Li_2O curve is even flatter.
Once again a certain regularity is present, which , however, is
conditioned by other factors than those in the first area.

In the third area, finally, the curves bend back over.
The maximum values of the potentials seem to have been reached
here or at somewhat higher R_2O concentrations. On this somewhat
unexpected course of the curves at higher concentrations a new
influence appears, which can be easily interpreted and is
therefore discussed first.

a) <u>The effect of the dissolution of the crucible material
on the potentials</u>. During the measurement of the alkali content[3]
it was discovered that the melts with low and medium alkali
content dissolved clearly in water, while those melts with high
alkali content did not. An insoluble residue remained to be

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[3] Only that fraction of the melt was investigated which was found
immediately about the electrode.

determined. It was undissolved crucible material (Al_2O_3, SiO_2). Table 4 shows how much insoluble material was observed in a sample of melts.

TABLE 4. MELTS WITH COMBINATIONS ALTERED BY CRUCIBLE DISSOLUTION

K_2O borate	Na_2O borate	Li_2O borate
Melts with 7.75 mol-% K_2O	Melts with 14.9 mol-% Na_2O	Melts with 21.5 mol-% Li_2O
Contained traces of (Al_2O_3 and SiO_2)	Contained traces of (Al_2O_3 and SiO_2)	Contained 2.10% (Al_2O_3 and SiO_2)
Melts with 19.5 mol-% K_2O	Melts with 33.1 mol-% Na_2O	Melts with 45.2 mol-% Li_2O
Contained 1.9% (Al_2O_3 and SiO_2)	Contained 3.05% (Al_2O_3 and SiO_2)	Contained 2.70% SiO_2 and 3.36% Al_2O_3
Melts with 37.4 mol-% K_2O		
Contained 4.5% (Al_2O_3 and SiO_2)		

As can be seen from the potential curves, the appearance of these impurities with the decrease in potential is parallel for all three series, as can be expected if Al_2O_3 and SiO_2 are present in the melts or acids. Especially remarkable, in their phenomenon in the lithium melts. While the curve runs completely straight between approximately 4 to 18 mol-%, it then bends noticeably down. It is striking that in the sodium glasses the potential of the final melt (38 mol-%) is lower than that of the melt before the last with approximately 33 mol-% Na_2O. This can only be explained as a result of the dissolution of the crucible. It is probable that the potential for the melt with 33 mol-% Na_2O was also charged a bit too low, since the

dissolution had already begun here, though to a lesser extent.
All the same, the melt richest in potassium with 37 mol-% K_2O
yielded too low a potential for the same reasons; likewise, though
to a lesser extent, the melt with 30 mol-%. In order to
compensate for the effects of the crucible material in the
high basic melts, which are unavoidable in the present arrangement,
extrapolated curves are added to Fig. 8 and signified by
dotted lines in the high alkali area. These seem to come closer
to the true properties than the values actually measured.

This extrapolation, which may appear at first to be
capricious is further justified by the indicator experiments
discussed in Section D below.

b) <u>The relation between the molecular structure of the
borate glasses and the potential curves</u>. Before a quantitative
interpretation of the potential curves is attempted, the typical
course of the potential curves is explained qualitatively
according to the constitution of the melts. According to the
X-ray crystallographic studies of J. Biscoe and B.E. Warren [39]
the pure B_2O_3 could be conceived of as being built up from
BO_3 groups, in which each O" ion belongs to two B^{+++} ions, i.e.,
they build a so-called oxygen bridge. These BO_3 groups build
a laminary network of great stability. This explains e.g., the
slow electrical conductivity, the relatively high viscosity and
the poor crystallization capacity of a B_2O_3 melt. If Na_2O is
introduced into such a melt, the tricoordination is converted
into a quadrant coordination. The BO_4 groups build a spatial
network comparable to the SiO_4 groups in SiO_2, which is likewise
very stable. Na^+ ions are in the cavity of this network. This
process continues with increasing sodium content until approximately
17% Na_2O. If the sodium content is increased further, the
network splits and decomposes into smaller building blocks (ion).
It is probable that the fundamental path of the curve of the
potential dependent upon the alkali content (Fig. 8) can be
related to these molecular processes (see below).

<u>connections</u>. It follows from the above that the molecular
state of the melts in the three distinguished alkali ranges is
quite different: in the area of low alkali concentration there
is a strong connection of B_2O_3 to BO_3 or BO_4^- groups followed by
a transitional range and then by a condition of high disassociation
in the area of high alkali content. We will first view the
latter area closer.

According to Fig. 8 there is clearly a tendency for the
potential curves to approach one another and an absolute value
with further increases in the alkali content. If this is assumed
for the order of magnitude of 1.2 V, then it is reached closest
by the potassium borate, while the lithium melts in contrast,
show a great deficiency. The differing behavior of K, Na, and
Li is controlled by two factors: 1. By a differing oxygen ion
concentration (disassociation) in K, Na and Li melts of equal
molarity; 2. By secondary factors such as diffusion potentials.
Diffusion potentials are determined by the different travel
velocities U and V of the concerned cations and anions. At
present there are no parameters given for the travel velocity in
glass melts, and therefore, a quantitative evaluation is not
possible. And even if it cannot be expected that the U and V
are approximately equal for Li^+ or Na^+ or K^+ and BO_2^-, nevertheless,
they are not greatly different in the region of almost complete
dissociation. Therefore, the diffusion potential is probably
insignificant. Hence, the assumption that the potential
differences of a few tenths of a volt between the K, Na or Li
glasses in the region above approximately 25-30 mol-% alkali is
determined by the oxygen ion concentration is not justified. This
means, however, that the potassium glasses (with higher C_O'') are
more basic than the corresponding sodium glasses and these in
turn are more basic than the lithium glasses (with the smallest
C_O''). In other words: in the potassium melts the possible

connections are electrolytically the most dissociated, in the lithium melts the least. This result presents an immediate analogy to the experiences in water solutions.

d) <u>Checking the basicity relations in alkali-rich regions with a color indicator</u>. It seems worthwhile to recheck these conclusions with a color indicator. It was not easy to find an indicator which would change at 850°C at the hoped for intervals. Iron oxide, chrome oxide, etc were, when melted in the air, completely present in their higher degrees of oxidation and could not be brought to a change even with strong acidification; the oxides would fall out and opacify. The change in manganese oxide occurred too far in the basic region. Sulfur, however, proved to be a suitable indicator with a transition of:

<div align="center">
polysulfide (brown) $\rightleftarrows$ sulfur (blue)

basic   acidic
</div>

The melts were colored in the following way: the dye-free glass was melted from measured amounts of boric acid and potash or B_2O_3 and Na_2CO_3, etc at 850°C; a grain of $Na_2S\cdot9$ aq corresponding to approximately 0.2-0.3% Na_2S (related to the completed melt) was then quickly added and the melt placed in the oven for another 15 minute for temperature equalization. The platinum crucible was then taken from the oven, the melt taken out and then cooled between two iron plates. The alkali content of the melt was systematically varied and the interval of change narrowed. The change from brown (polysulfide) to gray (mixed color) to blue (free sulfur) was relatively sharp and could be reproduced well. The total interval of change lied within a 3% alkali variation so that the change median (gray) was correct to within 1 to 2%.

In the 3 alkali borate series the sulfur change points at 850°C lied as follows:

Melt	Color change brown ⇄ blue at
Potassium borate	25.5 mol-% K_2O
Sodium borate	27.5 mol-% Na_2O
Lithium borate	36.5 mol-% Li_2O

Melts with these connections must have the basicity at 850°C. If one finds in Fig. 9 (inset from Fig. 8) the EMF values of these combinations on the corresponding curves, it is clear that in the potassium and sodium glasses practically the same potentials of 0.83 V are given; in the lithium the corresponding potential value lies at 0.7 V on the actually measured curve (dotted in Fig. 9), while the extrapolated, more probable curve has an EMF value of 0.85 V, practically the same as the K and Na. That the 3 given melts -- potassium, sodium and lithium -- of equal basicity yield practically the same potential (against B_2O_3 as control melt) implies that the oxygen ion concentration used as a measure for the basicity in the observed region of alkali-rich melts was correctly grasped by the EMF. The suggestions in the previous section and the extrapolation of the lithium curves are justified and confirmed here.

    e) <u>Estimation of the degree of disassociation of the melts in the high alkali region</u>. At present no parameters have been given for the degree of electrolytic disassociation of glass melts. Since no secondary factors (diffusion potentials) were found to be noticeable in the region in question, the degree of disassociation /358 of the melts can be estimated if two assumptions are made. The first presupposition is that the potassium borate glass is completely disassociated in the combination of KBO_2 (50 mol-% K_2O) (this is only true for large quantities); secondly, the maximum EMF value is reached at about 1.2 V. The potentials of the chain

    +Pt/KBO_2 melts/ K or Na or Li borate melts/Pt -- can be converted according to the O" concentrations using the Nernstein relation

$$E = \frac{RT}{nF} \cdot \ln \frac{c_0''}{c_0''} ,$$

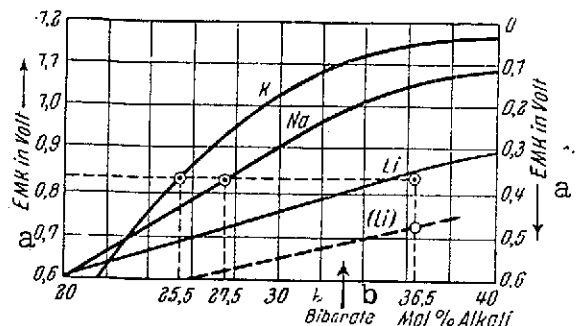in which n = 2, c_0'' = the sought after concentration and C_0'' = the concentration of the KBO_2 melt.

Fig. 9. Inset from Fig. 8.
The points of change of
the sulfur indicator are
given.

Key: a. EMF in volts
     b. Diborate

The following EMF values can be found in Fig. 9 from the right-hand ordinates for the combination 33% R_2O, 67% B_2O_3:

Potassium glass	0.08 V
Sodium glass	0.20 V
Lithium glass	0.40 V

The following would then be disassociated from the added alkali oxides in free, electro-motor active O" ions: in potassium diborate glass 33% of the present K_2O in sodium diborate 2.5% of the present Na_2O, in lithium diborate glass 0.04% of the present Li_2O.

These figures are surprising, especially because of the seemingly so small disassociation of the sodium and lithium melts. For the moment these parameters should be taken with great reservation, since it is by no means certain if the assumptions are correct.

f) The potential curves in the region of low alkali content. The interpretation of the the potential curves in the region of low alkali content is more difficult. This is a region of high viscosity and the hindrance of the mobility of the cations and of the O" anions must be reckoned with.

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When it is assumed that the free oxygen ions can be electromotively active the hindrance of the ion travel by the increase in viscosity should extend equally for both types of ions. It is not necessary for a noticeable diffusion potential to appear if the combinations of the two melts united in the chain do not lie too far from one another. If, however, these assumptions are incorrect, then a powerful diffusion potential must appear, since the mobility of the cation and the O" ion ("giant anion") found on the network are quite different. To answer this question the expanded Nernstein formula must be used. Since all measurements have shown that the "thinned solution," i.e., the melts with a low alkali concentration build the positive pole, the chains in this region clearly are those in which the anions are electromotively active. The equation would then be:

$$E = \frac{2U}{U+V} \cdot \frac{RT}{nF} \cdot \ln \frac{C_0''}{c_0''}$$

in which U and V are the travel velocities of the cations or anions, n = 2, C_0'' is the O" concentration in the alkali-rich melts, c_0'' is the O" concentration in the alkali-poor melts, i.e., B_2O_3. The equation can be simplified by allowing U + V = 1, that is only U, the relative travel velocity of the cation remains in the formula. Attention is turned to the potassium curve, which has an EMF value of practically zero up until about 10% K_2O. If this behavior is to be explained in view of the above formula, it must be assumed that one of the factors is zero. It can be either that

U = 0 or $\ln(C_0''/c_0'') = 0$.

It is inconceivable that the travel velocity of the cation (K^+) is zero after it is known that the alkalies can be thoroughly electrolyzed at low temperatures through glass. The other possibility, that $\ln(C_0''/c_0'') = 0$ would mean that $C_0'' = c_0''$.

In other words, with the introduction of K_2O up to 8 mol-%
the O" concentration can show practically no increase. This
can be explained on the basis of the conception of the molecular
structure of these melts (see above). With the introduction of
K_2O in B_2O_3 the [BO_3] group is transformed to [BO_4] and the
relatively large and only singly-charged K^+ion is, because of its
weak field intensity not capable of separating O" ions from the
stable BO_4 groups in any noticeable quantity. Only when the
BO_4 network is made unstable by sufficient K_2O (>10%) does it
disintegrate; and then with a fast increase of C_O" and with it
of the EMF.

The sodium borate curve appears very similar to the potassium
curve in its total path except that the EMF climbs about 0.3 V
within the first few percentages of Na_2O (against B_2O_3) and then
climbs only weakly until 7 or 8% Na_2O. With an increasing
alkali content, however, the EMF curve also begins to climb more
steeply, if not as steep as by the potassium glasses. The
radical climb of the EMF curve with the smallest addition of Na_2O
to B_2O_3 can be interpreted as an effect of the greater field
intensity (smaller ion radius!) of the Na^+ ions as compared to
the K^+ions. That is, the Na^+ is capable of separating the
individual O" ions from the BO_4 network so that an oxygen ion
concentration is created, which is much greater than in B_2O_3 or
a corresponding potassium glass. This interpretation would also
explain why the BO_4 network breaks up earlier with the addition
of Na_2O than with the addition of the same amount of K_2O.

This property is even more noticeable with Li_2O, which
clearly shows an analogous process of breaking down through the
climbing of the potential curve at 2-3 mol-%. This is explained
through the even greater field strength of the Li^+ compared to
the Na^+.

The path of the 3 curves in this region of low alkali content yield some interesting consequences for the basicity. If the EMF values are a true expression of the concentration of free O'' ions, then the lithium melts must be more basic than the equimolar Na and K glasses at lower alkali contents and 850°C.[4] /359

On the basis of the probable but undemonstratable assumptions, these conclusions from the electrochemical measurements are not in themselves convincing. Therefore, a color indicator was sought which would change in this region of low alkali content. CoO was shown to be suitable for this. As is known, it colors rose-red in pure boric acid according to W. Weyl [41]. The Co cation can be conceived of as almost completely "solvated." With increasing alkali content it is transformed to an anionic blue complex. In the production of, e.g., borate glasses with 10 mol-% alkali and 0.5% CoO, the following coloration can be observed.

> Potassium glass almost pure red; blue tint hardly noticeable,

> Sodium glass, blue tint more noticeable than in potassium glass,

> Lithium glass, clear red-violet.

It follows that in this region the lithium glass is actually more basic than the Na or K glass, i.e., the inverse of the (usual) region of higher alkali concentration. This also justifies the assumptions made about the action of the $C_{O''}$.

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[4] These consequences are expressly valid for the temperature of 850°C (and probably lower); at higher temperatures, the curve intersection point (Fig. 8) moves toward the left.

We can now return to the above-discussed studies of Peddle of the solubility of lead glasses with various alkali contents. It was shown in glasses with 20-25 mol-% alkali the potassium behaved significantly more basic against the sodium than in half as much alkali contents. The K_2O is, therefore, no longer as strong a base in low-alkali contents as in high alkali contents. This change in the base strength in K_2O agrees fundamentally with the observations made with the color indicators and the interpretations of the potential measurements.

g) The potential curves in the region of medium alkali content. Corresponding to the inversion of the order of the basicities of Li, Na and K glasses during the change from lower to higher alkali contents, and vice versa there must naturally be an intersection of the potential curves in the region of transition, i.e., in the region of medium alkali content. As can be seen in Fig. 8, the curves meet practically in a single point. One is tempted to give this point a particular significance. At present it is not possible to say whether it has a deeper meaning or what that meaning might be. It has been shown, though, that with increasing temperature this point moves to lower alkali contents. It can be seen in Fig. 5, for example, that the 3 glasses at 1100°C have the same gray content and therefore basicity if the alkali content is about 8-10 mol-% (as compared to about 22 mol-% at 850°C). This corresponds to the idea that the breakdown of the network can be affected not only through the decrease of the alkali content, but also through the increase of temperature. On the other hand, insofar as one can see from the extrapolation of the Na and K curves the curves of the 3 alkali glasses do not seem to intersect at one point. This interesting question deserves further investigation.

Further conclusions or a closer evaluation of the potential curves appears, for the moment, to be uncertain. In particular, there is a need for measurement of the ion travel speeds in order to get an overview of the effects of the diffusion potentials. If, in addition, the disassociation, i.e., the C_0'' of the pure boric acid or of a given borate at 850° is known, then the absolute values for the oxygen ion concentration throughout the entire range can be calculated and the absolute basicities, that is the p_0'' values in analogy to the p_H numbers of the water solution can be determined. Of course such measurements would involve serious experimental difficulties.

IV. Conclusions

1. The meaning of the results for the constitution of the glass[5]

The EMF measurements of the various borate glasses together with the indicator experiments have shown that at lower alkali contents the basicity of potassium, sodium, and lithium borate glass increases given an equal mole content R_2O. Vice versa a decrease in the basicity in the same order can be observed at high alkali contents. At medium alkali contents there is necessarily an intersection of the values. This rather unique finding is explained in terms of the various field strengths of the alkali ions. The separation of the electromotive active O'' ions from the $[BO_3]$ or $[BO_4]$ network at lower alkali contents is achieved most easily by Li and is most difficult for K. Since this observation is made independently of the possible transformation in the borates of $[BO_3]$ to a $[BO_4]$ network analogous properties can be expected in silicate glasses. W. Weyl [42] has explained the remarkable properties of the lithium glasses vis-a-vis viscosity, crystallization capacity, etc. in comparison

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[5] This Section I will be included at the end of this dissertation.

to Na and K glasses as a result of the increased field tension, which expresses itself in the building of more or less highly "associated" molecule complexes. We can now go further and say that not only does a variably strong breakdown of the R-O-R bridges and the building of mobile R-O-Li groups follow, but also that the O" ions are disassociated through various degrees.

In the region of high alkali content the network is, to a large extent, divided into small complexes, the simplest case being that of the RBO_2 molecule. The oxygen ion concentration here is determined by the degree of disassociation in $R\cdot + BO_2'$, which must be smaller in the higher field strengths of $Li\cdot$ than e.g., in $Na\cdot$ or even more so in $K\cdot$. These conclusions can widen our previous ideas about the constitution of the glasses and make possible assertions about the properties, which can be deduced from the glass structure. In particular, the division and disassociation processes can be pursued in terms of the viscosity. It has already been stated, that in agreement with /360 our idea of the constitution of these glasses at normal alkali concentrations, the lithium glasses are the most fluid and the potassium glasses (at an equal mole content) are the most viscous. It must therefore be expected that at higher alkali contents the potassium glasses would be more fluid, since they contain smaller fragments ($K\cdot + BO_2'$ or $SiO_3"$), while the lithium glasses must be more viscous as a consequence of their lower disassociation ($LiBO_2$) and the probably stronger "formation cluster" of the $Li\cdot$ ion. The consequences drawn from the present electrochemical study agree excellently with the results and their theoretical interpretation made on the basis of more elaborate and systematic viscosity measurements in the newly published work of K. Endell and H. Hellbrügge [43]. Fig. 10 shows the viscosities determined in this work for alkali silicate glasses of various alkali contents at 1300°. As can be seen, the lithium glasses are more viscous than the potassium glasses at higher alkali contents.
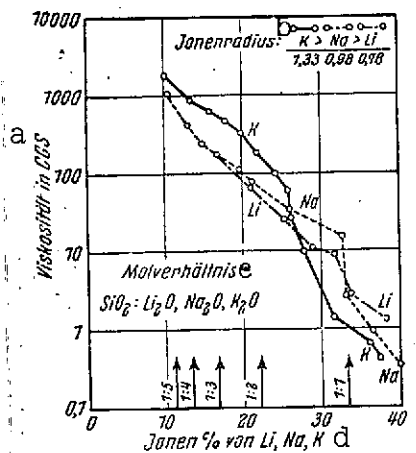
Fig. 10. Viscosities of
Li, Na and K silicate glasses
plotted against alkali content
(expressed in ion percentages)
at 1800°. From K. Endell and
H. Hellbrügge.

Key: a.   Viscosity in CGS
        b.   Ion radius
        c.   Mol ratio
        d.   Ion percentages of
              Li, Na, K

The agreement of the
results of two totally
different observation
processes increases the
certainty of the assertions
of both methods. It has
thereby been shown that the
electrochemical procedure
is a valuable tool for
increasing our knowledge of
the constitution of glasses.

2.   The supposed position
of the neutral point.

We now return to the
question posed at the
beginning of this work,
whether or not it was necessary
to assume the presence of acids
and bases in glass melts and
if so, where the neutral point
would lie; further, whether

the solvent material would appear in a neutralization reaction
as in aqueous solutions. It was determined that SiO_2, B_2O_3, P_2O_5,
etc should be viewed as acids in agreement with the current
usage. The analogy to water as a solvent is unsatisfactory. The
question now is, where between the acid and the bases does the
neutral point lie? Along with this it must be asked, in what
region -- acidic, "neutral" or basic -- do the usual technical
glasses lie?

In reference to the problem of determining the position of the
neutral point the following facts are mentioned. The pure acids
are electrolytically very weakly dissociated, as can be seen, for
example, from the low specific electrical conductivity of B_2O_3

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or SiO_2 and the given EMF curves. The same is true for the
pure bases; they are also weakly dissociated as can be seen from
the high melting point of alkali earth oxide. Pure, water-free
alkali oxides also appear, as far as is presently known, to
possess such high melting points (e.g., Li_2O above 1625°C
according to F. M. Jaeger and van Klooster, Na_2O above 1750°C
according to Bailey [44]). Between these two extremes is a
region of melts of good conductivity and high dissociation, i.e.,
high oxygen ion concentration, which, as has been shown in the
present work increase radically from the acidic side and which
clearly tends to a limiting value in the region of about 50-60 mol-%
alkali in the case of boric acid. This limiting value must be
a maximum value, since the dissociation against the pure base must
again decrease. Most probably the neutral point can be found in
the combinations with the highest oxygen ion concentration.

It follows, then, that all the usual glasses lie in the
acidic region. An immediate comparison can be made with the
manganate ion, which, as is known, disintegrates in a aqueous
solution as soon as the solution is acidified. The glass behaves
analogously. At the transition to the acidic region, which
clearly begins in the neighborhood of its transformation point)
it decomposes under the separation of oxygen and the building of
Mn^{III}.

The di- and tetrasilicates should be seen as acidic salts,
somewhat analogous to NaH_2PO_4 or $NaHSO_4$ etc. Sodium orthosilicate
would be (to be determined by experiments with the manganate
indicator) either somewhat neutral or already somewhat basic
(comparable to Na_3PO_4 in an aqueous solution). Further studies
of this -- according to present usage -- "highly basic," in
actuality somewhat neutral, region must be undertaken to obtain
some clarity.

As far as the solvent is concerned there is no clear analogy to water in the melt flow and the neutralization reactions occur according to the following scheme:

acid + base = salt.

The solvent must be understood as the entire melt and not as individual groups of molecules.

V. Summary

1. It is usual in writings about glass technology and ceramics to speak of "acidic" and "basic" glasses and tones or masses. These concepts, however, are no longer sufficient for the technically useful region of combinations. The question of a neutral point also remains open. The present work was intended to study the basicity relations in a few simple glass systems.

2. The present definitions of "acids" and "bases" are not satisfactory for glasses or melted salts. Neither the formulation according to Arrhenius nor according to Brönsted nor according to Wickert is usable in the present system, since by definition the glasses contain no "water-like" solvent. The formula used by Lux for the oxidic system in analogy to the Brönstedian:

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acid + O" = base
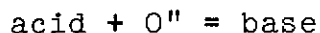
is only sufficient to give the order of basicity. It is not possible here to determine if a melt is acidic or basic or where an actual neutral point would lie.

3. There are three possibilities for an interpretation of the basicity relations in the glasses:

a) glasses are a mix of melted salts without a decidedly acidic or basic character. This explanation is untenable, since

numerous reactions which can only be explained through the activity of acids or bases can be introduced as examples.

b) SiO_2, B_2O_3, etc take over the role of the neutral solvent in glasses (analogous to H_2O) and the usual glasses with alkali, etc lie more or less far in the basic region. This view was tested according to measurements of conductivity and potentials obtained within the framework of attempts to find a suitable acid for this system (e.g., BF_3, BPO_4, etc). All the results speak against the activity of SiO_2, B_2O_3, etc as a solvent.

c) SiO_2, B_2O_3, P_2O_5, etc are the glass acids. For this case, which best agrees with the actual properties of these materials the question of where a neutral point between the acids and bases would lie and how the acid and bases can be distinguished according to their "strength" still remains.

4. The deeper meaning of the basicity relations in the glass building material systems is shown in a series of phenomena. It can be shown that there is an inner connection between the highest silification grade of a basic oxide in the known crystallized silicates (e.g., $K_2O \cdot 4SiO_2$, but $Na_2O \cdot 2SiO_2$ or $CaO \cdot 1SiO_2$, etc) and the "strength" of this base, i.e., its ability to bind acids. In view of the numerous silicate systems a meaningful ordering of the basic oxides according to their strength can be made; the strongest known base in glasses today is K_2O (or Rb_2O). Similar connections obtained between the basicity of glasses and the fluxing power, water solubility and absorption of gas.

Though uncommon up to now a magnate ion was used as an indicator for the alkali rich glassy solidifying combination.

5. With the aid of color indicators the basicity of the following material systems were compared at a melting temperature of 1100°C and with air as the melting atmosphere:

$K_2O - SiO_2$	$K_2O - B_2O_3$	$K_2O - P_2O_5$
$Na_2O - SiO_2$	$Na_2O - B_2O_3$	$Na_2O - P_2O_5$
	$Li_2O - B_2O_3$	

It was discovered that SiO_2 was the weakest acid; B_2O_3 is significantly stronger, and the strongest is P_2O_5. Among the bases in the region of usual alkali content Li_2O is the weakest, K_2O is the strongest.

Lines of equal acidity of the melts (isoacids) can be drawn in a diagram, thereby giving a simple overview of the relations.

6. To determine the strength of the ion concentrations determining the basicity in the melts galvanic chains of the type
+Pt(air)/B_2O_3/borate melt/Pt(air) -- were built. For the systems Li_2O - B_2O_3, Na_2O - B_2O_3, K_2O - B_2O_3 characteristic potential curves in the region of 0-40 mol-% alkali at 850°C were obtained, which were then interpreted according to the present conceptions of the constitution of these glasses. It is noteworthy that the oxygen is electromotively active according to the polarity of the chains -- as was expected. The observed electromotive forces of these chains are quite remarkable (until over 1 V).

7. In the course of the potentials as plotted against alkali content two significant regions could be distinguished, not including the transitional region. Above approximately 22 mol-% alkali, that is, in the region of "normal" alkali

content (e.g., with borax) the EMF values for the potassium glasses (placed against B_2O_3) lied above those of the sodium and lithium glasses. This means that the O" ion concentration and thereby, the basicity of the alkali borate melt increases in the order Li, Na, K. This result was confirmed through a comparative test with a color indicator (sulfur).

According to the potential measurements this order is reversed in the region of low alkali contents, the lithium glasses are the most basic here, the potassium glasses the most acidic. This too was confirmed through the use of a color indicator (CoO).

This diversion was explained by noting that at lower alkali contents, the electromotively active O" ion can more easily be torn from the immovable network by the small Li^+ ion than by the large K^+. At higher alkali contents simpler constructions are present, for example, RBO_2 molecules; C_O" is essentially determined then by dissociation, which in the case of potassium glass is greater than with sodium glass.

This expanded view of the constitution of the glasses is confirmed by the interpretation of measurements of the chemical resistance capacity and agrees with the newest results of viscosity measurements and their interpretation by K. Endell and H. Hellbrügge.

8. A calculation of the absolute oxygen ion concentration cannot be accomplished because of the possibility of the appearance of diffusion potentials, especially in the region of medium and lower alkali content. In addition, a knowledge of the C_O" for B_2O_3 is still lacking.

9. As the alkali content increases, the potential curves seem to approach a limiting value, which is probably also a

maximum value for the $C_{O''}$ corresponding to the neutral point <u>/362</u>
between acid and base. All the remaining glasses are, therefore,
in the acidic region. Di- or tetrasilicate can be formally
grasped as acidic salts.

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